

The fate of heavy metals in landfills: A Review

by

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1. Introduction and background

Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems. Nevertheless, because of certain useful physical and chemical properties, some heavy metals, including mercury, lead, and cadmium, are intentionally added to certain consumer and industrial products such as batteries, switches, circuit boards, and certain pigments. Usage patterns of heavy metals in products have varied over the years. Mercury was once widely used in pharmaceutical products, agricultural chemicals, dry cell batteries, and paints. Many of these uses have been phased out, although others continue, e.g. chlor-alkali production, switches and electrical apparatus, fluorescent light bulbs, and dental amalgam. These ongoing uses of mercury too are declining. In 2004, world mercury production was estimated to be 1260 metric tons per year, which was significantly less than the 2200 t/y average world mercury production from 1990 to 2000.¹

Cadmium was at one time widely used in electroplating processes to coat iron and steel. By the 1940s, electroplating represented about three-fourths of cadmium consumption. Production and consumption of cadmium in the U.S. peaked in 1969, at approximately 6,000 tons per year.² In recent years, cadmium has been used increasingly for the production of rechargeable batteries, and this is now the dominant use of the metal. Although production and consumption of cadmium in the U.S. have declined, these reductions have been offset by increased uses in other regions. Globally, cadmium consumption is reported to have increased by about 1% in 2003 vs. 2002, with China the leading cadmium consumer.³ Despite efforts to increase the recycling of consumer items that have rechargeable batteries containing cadmium, it is likely that many such consumer items ultimately enter the municipal waste stream.⁴

In some cases, at least partial releases of heavy metals to the environment during the normal life cycle of the product occur. In other cases, while the heavy metal may be contained during product life, management of discarded products leads to significant releases to the environment. An example of the latter type of release is the volatilization of mercury from automobile convenience light switches when recycled ferrous metal containing such switches is melted.

¹ Brooks, William E., 2004, Minerals Yearbook: Mercury, U.S. Geological Survey, 2004, from <http://minerals.usgs.gov/minerals/pubs/commodity/mercury>, downloaded 11/15/05.

² Plachy, Jozef, 2000, Minerals Yearbook: Cadmium, U.S. Geological Survey, 2000, from <http://minerals.usgs.gov/minerals/pubs/commodity/cadmium>, downloaded 11/15/05.

³ Plachy, Jozef, 2003, Minerals Yearbook: Cadmium, U.S. Geological Survey, 2003, from <http://minerals.usgs.gov/minerals/pubs/commodity/cadmium>, downloaded 11/15/05

⁴ Boehme, Susan and M Panero, 2003, Pollution Prevention and Management Strategies for Cadmium in the New York/New Jersey Harbor, New York Academy of Sciences, NY., www.nyas.org

Concerns about possible releases of heavy metals during a product's life cycle (from raw material extraction to disposal), or during recycling of a product containing a heavy metal, raise many questions. From the perspective of the optimal use of resources – isn't it better to recycle a heavy metal in products rather than continue to mine it? However, is it wise to recycle certain products when this recycling could, at best, merely return a heavy metal to commerce, affording additional opportunities for its release to the environment during product use, or, at worst, cause the release of significant quantities of the heavy metal to the environment during recycling operations? Obviously, substitution for other less toxic materials would be optimal since it would eliminate the cycling of the heavy metal, during use and recycling or disposal. In this case, the question remains - what to do with the products containing heavy metals that are already in commerce today and will be disposed of in the near future? A thorough answer to this question requires a comparison of the quantity of the metal that escapes to the environment during the course of different solid waste management options, including disposal and recycling (or recovery before disposal when the heavy metal's return to commerce is not advisable).

The method of disposal is typically either landfilling or incineration. The latter includes some open burning, which still occurs in rural areas of the U.S. via devices such as burn barrels. Releases of heavy metals to the environment may occur via volatilization upon incineration, open burning, or in the event of fires at landfills, transfer stations or recycling centers. Releases may also occur via landfill leachate. In New Jersey, about one third of MSW is incinerated, about one third is landfilled in-state, and the other one third goes to out of state landfills; the state's incinerator ash is typically landfilled, mixed with MSW.

Because an available and frequently used option for many products containing heavy metals is disposal in a municipal solid waste or hazardous waste landfill, this paper attempts to summarize available information on the fate of heavy metals in landfills. Other disposal options, such as WTE or open burning, are not investigated in this paper. Modern landfill design includes containment systems intended to prevent significant release of leachate and associated pollutants to surface or ground water. However, much waste has historically been disposed of in landfills or dumps⁵ with deficient or non-existent containment systems. Also, the performance of containment systems over relatively long time frames, e.g. hundreds to thousands of years, is unknown. Because a typical landfill may contain, at capacity, millions of tons of waste, which could contain heavy metals at concentrations of several parts per million or more, a typical landfill could contain thousands of kilograms of heavy metals.⁶ Understanding the likely long-

⁵ The term "landfill" is herein used to represent a land disposal facility that places waste in layers and covers this waste daily with materials such as earth to isolate it to some degree from the environment. In the past, much waste was simply piled as high as feasible in disposal locations, and sometimes periodically ignited to reduce volume.

⁶ New Jersey's more than 500 known and suspected landfills (most of which are no longer active) contain in the vicinity of 475 million cubic yards of waste, according to the Volume III, page 156 of the NJ Mercury Task Force Report, January, 2002, NJDEP, Trenton, NJ. This same reference indicates that based on data available at the time it was estimated the mercury content of waste in place was 2.5 ppm and that,

term fate of these metals is important in evaluating the various management options for products containing heavy metals.

Unfortunately, reliable analytical techniques and adequate sampling of media containing potential releases from waste disposal sites are only decades old, and so meaningful long-term data on the fate of heavy metals in wastes do not exist. Because of the potential toxicity of heavy metals when introduced into the environment, the ability of landfills to sequester them over long time spans is essential if landfills are to be truly considered as acceptable disposal sites for metal-containing wastes.

2. Quantities of heavy metals in MSW

Because of their toxicities, heavy metals have been singled out for concern as environmental pollutants. In addition, and given the documented toxicity to organisms, certain metals, termed “RCRA heavy metals”, have specific groundwater limits pursuant to the U.S. Resource Conservation and Recovery Act (RCRA). These metals include arsenic (As), Barium (Ba), Cadmium (Cd), Chromium (Cd), Lead (Pb), Mercury (Hg), Selenium (Se), and Silver (Ag). Other heavy metals such as Nickel (Ni), Copper (Cu), and Zinc (Zn) are also of concern. These metals are apparently not RCRA metals because at low levels they function as nutrients and also because they have not shown human toxicity to the same degree as the RCRA metals. However, they can be toxic to other organisms, and in some situations to humans as well, and therefore are included in this review.

Several studies have provided data on quantities of heavy metals in MSW. Table 1 below shows quantities of heavy metals estimated to be disposed per year, in some cases as directly reported and in other cases based on reported concentrations multiplied by an estimated yearly quantity of 250 million tons metric tons MSW disposed of in landfills.⁷

since a cubic yard of compacted waste has a weight of approximately 450 kg, the waste in place in New Jersey contained approximately 500,000 kg of mercury. Similar or perhaps greater quantities of other heavy metals are likely also present in landfills.

⁷ Goldstein, Nora, and Celeste Madtes, 2001, 13th Annual Biocycle Nationwide Survey: The State of Garbage, *Biocycle*, December, 2001. The authors report that their survey showed 409,029,000 tons MSW generated in 2001 in the U.S., and that 61% of this was landfilled.

Table 1. Heavy metals in MSW

Metal	Estimated MSW concentration	Metric tons/year disposed of in U.S. landfills, either as reported directly or assuming 250 million tons MSW disposed/year and concentration as in column to the left
Cadmium (Cd)	4 ppm ⁸	1000
	20 ppm ⁹	5000
		2700 ^{10,11}
Copper (Cu)	77 ppm ¹²	19,250
Chromium (Cr)	350 ppm ¹³	87,500
Lead (Pb)	230 ppm ¹⁴	57,500
	400 ppm ¹⁵	100,000
		127,000 ¹⁶
Mercury (Hg)	1.5 ppm ¹⁷	375
		400 ¹⁸
Nickel (Ni)	57 ppm ¹⁹	14,250
Zinc (Zn)	380 ppm ²⁰	95,000

⁸ Prudent, P., M. Domeizel, and C. Massiani, 1996, Chemical sequential extraction as a decision-making tool: application to municipal solid waste and its individual constituents, *Science of the Total Environment*, 178, 55-61.

⁹ Aucott, M., 2005, Based on review of data submitted to NJDEP Division of Solid and Hazardous Waste and calculations based on those data by M. Aucott, NJDEP, Division of Science, Research & Technology, Trenton, NJ 08625.

¹⁰ Solid Waste Association of North America (SWANA), 2004, *The Effectiveness of Municipal Solid Waste Landfills in Controlling Releases of Heavy Metals to the Environment*, prepared for the SWANA Applied Research Foundation Disposal Group Subscribers. These data are based on interpretation of data provided by the USEPA.

¹¹ Franklin Associates, 1989, Characterization of Products Containing Lead and Cadmium in Municipal Solid Waste in the United States, 1970 to 2000, EPA 530-SW-89-015C, as referenced in Boehme, S. and M. Panero, 2003.

¹² Prudent, et al., 1996

¹³ Prudent, et al., 1996

¹⁴ Prudent, et al., 1996

¹⁵ Aucott, 2005

¹⁶ SWANA, 2004

¹⁷ Aucott, 2005

¹⁸ SWANA, 2004

¹⁹ Prudent, et al., 1996

²⁰ Prudent, et al., 1996

Per capita residential refuse discard rates appear to have remained relatively steady since 1980; in the earlier years of the 20th century, rates were higher, and the composition of the waste was different, with more fuel ash and less paper and plastic than in more recent years.²¹ Also, it is known that higher concentrations of certain metals existed in MSW in the past. For example, earlier, mercury was likely present at a concentration of about 4 ppm in MSW²² as compared to approximately 2.5 ppm or less in recent years. It seems likely, therefore, that quantities of heavy metals present in U.S. dumps and landfills is many times the current annual input rate.

Information on both the current concentrations of certain metals in MSW, and on recent trends in these concentrations can be gleaned from data reported to the New Jersey Department of Environmental Protection. These data include concentrations of total metals in incinerator ash, total quantities of ash produced, and total quantities of MSW incinerated. Emissions of the volatile metal, mercury, from New Jersey MSW incinerators are also reported. Analysis of these data for one facility, the Essex County Resource Recovery Facility, permits an estimation of the overall concentration of cadmium, lead, and mercury over time in the MSW incinerated by that facility. These data indicate a relatively unchanged, but perhaps recently declining concentration of mercury in MSW over the last 15 years, a variable but essentially constant concentration of lead, and a noticeably increasing concentration of cadmium in MSW.²³

These data are pictured in Figure 1, 2, and 3, below.

²¹ Walsh, Daniel C., 2002, Urban Residential Refuse Composition and Generation Rates for the 20th Century, *Environ. Sci. Technol.*, 36, 4936-4942.

²² Themelis, Nickolas, and A. Gregory, 2001, *Sources and Material Balance of Mercury in the New York-New Jersey Harbor*, p. 27, Report to the New York Academy of Sciences, Oct. 3, 2001, Earth Engineering Center, Columbia University.

²³ Aucott, M., 2005, unpublished data analyzed by M. Aucott, New Jersey Department of Environmental Protection, Trenton, NJ.

Figure 1

Cadmium content of solid waste

Based on waste quantities and ash concentrations
at the Essex County, NJ MSW incinerator

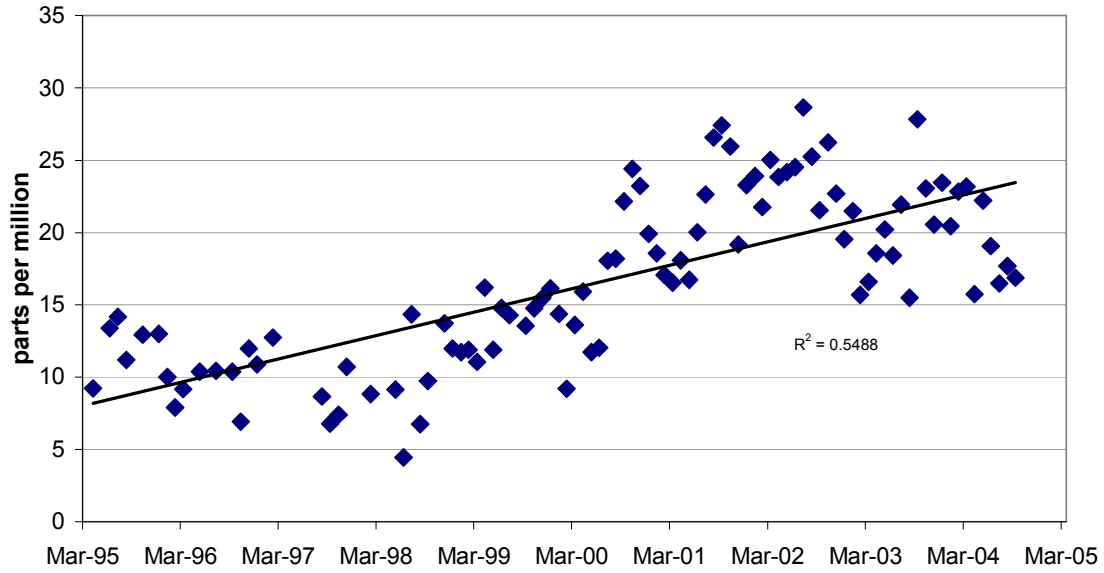
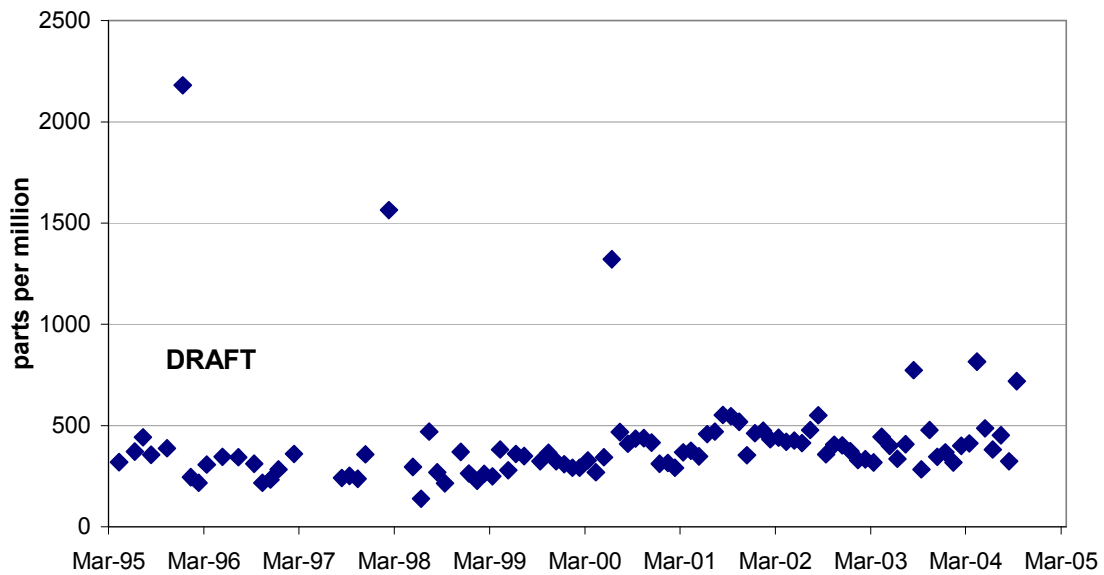


Figure 2

Lead content of solid waste

Based on waste quantities and ash concentrations
at the Essex County, NJ MSW incinerator



perhaps 75% of the cadmium in MSW today is in the form of batteries.²⁵ Prudent, et al. found that copper was mostly associated with non-ferrous metal or metal scrap but also was associated with fine particles, paper and cardboard (inks). They found that chromium was mostly in the form of non-ferrous metal scrap but perhaps 25% of the load in waste was in leather. Nickel was found to be mostly associated with scrap metal, but also with glass and fine particles. Zinc and lead were mostly in the form of scrap metal, but also were found associated with fine particles. More detailed information is available for lead. Estimates for the year 2000 are that 65% of the lead in products discarded in MSW was in the form of lead-acid batteries, 30% was in consumer electronics, and 4% was in glass, ceramics, and plastics.²⁶ Much of the mercury in waste is believed to exist primarily within disposed products including batteries, fluorescent bulbs, thermostats and other switches, and measuring and control devices such as thermometers.²⁷ A 2002 estimate for the waste from the NY/NJ harbor Watershed found that Dental amalgam waste from dental offices is a major mercury-containing input to MSW, contributing perhaps 50% of the total mercury in solid waste.²⁸

It is evident that the quantity of discarded consumer electronics devices has increased in recent years in MSW, raising questions about the fate of these devices in the landfill environment. They typically contain lead, cadmium, mercury, arsenic, copper, zinc and other heavy metals and rare earth metals.²⁹ As shown in the figure above, it appears that the quantity of cadmium in MSW has increased in recent years.

It is useful to speculate on the fate of heavy metals in the elemental form and in the form of compounds likely to form within landfills. Metals contained in glass or porcelain structures that manage to stay intact as they are placed in the landfill, and metals found within the matrix of certain plastics, glass, and ceramics, could remain unchanged in landfills for geological time spans. Other metal-containing materials are expected to be less inert. For instance, elemental mercury, found in items such as switches, could volatilize if the containment structure corrodes or breaks.

4. Characterization of the landfill environment: stages

The fate of metals and structures that contain them will be related to the properties of the environment in which they reside. There are a number of studies that have provided

²⁵ Boehme, Susan, M. Panero, Y. Rosenthal, and V. Thomas, 2003, *Pollution Prevention and Management Strategies for Cadmium in the NY/NJ Harbor Watershed*, New York Academy of Sciences, New York.

²⁶ USEPA, 1989, *Characterization of Products Containing Lead and Cadmium in Municipal Solid Waste in the United States, 1970 to 2000*, EPA/530-SW-89-015C, Washington, DC, January, 1989.

²⁷ New Jersey Department of Environmental Protection (NJDEP), 2002, *New Jersey Mercury Task Force, Volume III, Sources of Mercury in New Jersey*, p. 105, NJDEP Division of Science, Research & Technology, Trenton, NJ, January, 2002.

²⁸ C.de Cerreño, Allison, M. Panero, and S. Boehme, 2002, *Pollution Prevention and Management Strategies for Mercury in the New York/New Jersey Harbor*, New York Academy of Sciences, New York.

²⁹ SWANA, 2004, pp. 27-29.

insight into the biological, chemical and physical properties of landfill environments. It has been found that these environments change over time. There appear to be several well-defined stages in the life cycle of MSW once it is deposited in a landfill. One description of these stages, as presented in a recent report,³⁰ is as below:

Phase I: Initial Adjustment - Within a short time after the waste is deposited, a community of microorganisms builds up to a population sufficient to begin to significantly alter the waste.

Phase II: Transition – Transformation from the initial aerobic condition to an anaerobic environment takes place. A trend toward reducing conditions, in which elements or molecules gain electrons, is established as electron acceptors shift from oxygen to nitrates and sulfates. By the end of this phase, measurable concentrations of chemical oxygen demand (COD) and volatile organic acids (VOAs) appear in the leachate.

Phase III: Acid Formation – During this phase, some of the waste is hydrolyzed, i.e. it reacts with water producing soluble products. In this stage, anaerobic, acid-forming bacteria, now the dominant type, metabolize biodegradable organic matter in the waste producing VOAs. The resulting levels of VOAs lead to a lowering of pH, and tend to increase the load of dissolved metals in the leachate. Organic matter rapidly ferments during this stage.

Phase IV: Methane Production – Also referred to as the methanogenic phase, this period is characterized by the rise to dominance of another group of microorganisms, methane-producing bacteria. These convert the organic acids produced in Phase III to methane and carbon dioxide. A highly reducing chemical environment develops, resulting in the reduction of sulfates (SO_4^{-2}) to sulfide (S^{-2}). In one study, which included simulated MSW and simulated construction and demolition waste containing wallboard, it was found that wallboard was the major cause of hydrogen sulfide production, and that methanogenesis and sulfate reduction occurred concurrently.³¹ The pH rises as NH_3 neutralizes H^+ ions, leading to the depletion of VOAs and the increasing presence of ammonium (NH_4^+) ions. The pH is maintained in the neutral range, however, by bicarbonates (HCO_3^+), and this supports the continued flourishing of the methanogenic bacteria. The presence of sulfides and hydroxides (OH^-) favors the precipitation of metals.

Phase V: Maturation – In this phase, biological activity declines due to the depletion of readily-degradable organic matter and other nutrients. Gas production also declines, and concentrations of pollutants in leachate are lower than in previous phases.

Other researchers have characterized the life cycle of a landfill in slightly different ways.

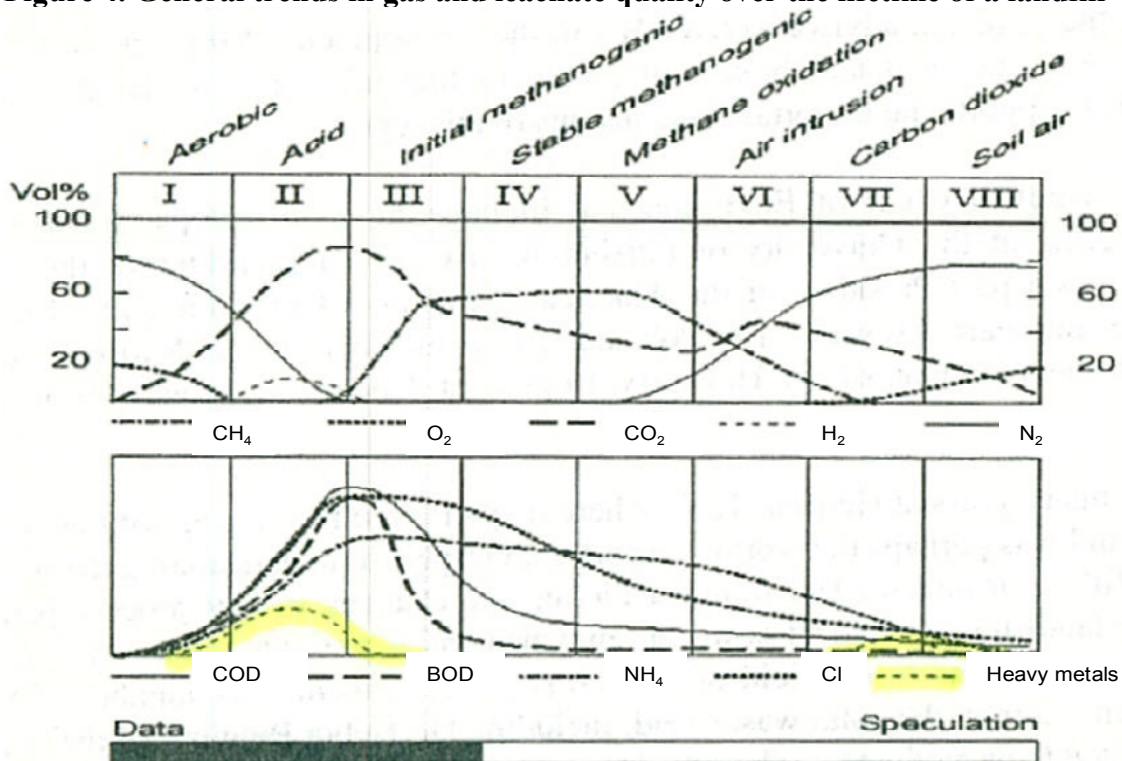
³⁰ SWANA, 2004, pp. 32-33.

³¹ Fairweather, Robert J., and Morton Barlaz, 1998, Hydrogen sulfide production during decomposition of landfill inputs, *Journal of Environmental Engineering*, 124, 353-361.

Kjeldsen, et al.³² describe eight phases. They lump phases I and II as described above into a single phase, the aerobic phase, and expand the methanogenic phase into three parts. They add three stages beyond this, the air intrusion phase, the carbon dioxide phase, and the soil air phase. See Figure 4., below.

It should be pointed out that not all agree that the general depiction of the life cycle of a landfill cycle as described above is valid for many of today's landfills. Landfills are typically capped when they are closed, which retards the entry of water. Further, many exist in relatively arid climates. These landfills may essentially be moisture-limited "dry tombs" that have different biology and chemistry than the older, often uncapped landfills that served as the basis for some of the understanding of landfill cycles as described.³³ [However, the description of the life cycle of MSW is likely to be typical of landfills in the Northeast region of the U.S., where the NY/NJ Harbor watershed is located.]

Figure 4. General trends in gas and leachate quality over the lifetime of a landfill



Copyright (2002) From Kjeldsen, Peter, M. Barlaz, A. Rooker, A. Baun, A. Ledin, and T. Christensen, 2002, Present and Long-Term Composition of MSW Landfill Leachate: A Review, *Critical Reviews in Environmental Science and Technology*, 32(4), 297-336. Reproduced by permission of Taylor & Francis Group, LLC., <http://www.taylorandfrancis.com>

³² Kjeldsen, Peter, M. Barlaz, A. Rooker, A. Baun, A. Ledin, and T. Christensen, 2002, Present and long-term composition of MSW landfill leachate: A Review, *Critical Reviews in Environmental Science and Technology*, 32, 297-336.

³³ Lee, G. Fred, 2004, Comments on "The Effectiveness of Municipal Solid Waste Landfills in Controlling Releases of Heavy Metals to the Environment," SWANA, 2004. From <http://www.members.aol.com/duklee2307/SWANA-heavy-metals-comments.pdf>, downloaded 8/15/04.

Noteworthy in the view of Kjeldsen, et al. are stages VI through VIII, the air intrusion, carbon dioxide, and soil air stages. These phases are postulated based on theory, and are expected to occur only after long time periods, perhaps hundreds or even thousands of years. In these phases it is projected that air will gradually intrude into the landfill,

bringing about the return of aerobic conditions. What little methane is still being produced in the first of these latter stages will be oxidized by the soil air before it escapes from the landfill. As the environment becomes more aerobic, more organic matter will be subject to oxidation. Some, so-called “recalcitrant” organic matter will likely remain, however. In the carbon dioxide stage, increasing concentrations of carbon dioxide from aerobic respiration could bring about a lowering of pH, as could the oxidation of reduced sulfur, nitrogen, and iron since these reactions release protons. There may still be buffering capacity, however, as metal carbonate precipitates would dissolve in this stage and this release of carbonates would buffer the pH.

5. Characterization of the LF environment: control systems, operation, and monitoring

Another important characteristic of a landfill is its pollution control system. Today’s landfills, pursuant to Subtitle D of RCRA, must include the following.³⁴

- 1) A liner that is composed of two different materials that separates the landfill and its contents from the soils and bedrock environment below. The upper layer of the composite material must be a synthetic flexible membrane liner (FML) that is at least 30 mil (i.e. 30/1000ths of an inch) thick. If the FML is high-density polyethylene, as is typical, it must be at least 60 mil thick.³⁵ The lower layer of the composite liner must be a 24-inch compacted clay liner that has a hydraulic conductivity of no more than 1×10^{-7} cm/sec, meaning that fluids cannot travel through it easily, and
- 2) A leachate collection and removal system that is sufficient to prevent the depth of the liquid layer (i.e., leachate) above the composite liner from reaching any more than 12 inches.

The purpose of the liner is to prevent leachate from mingling with the underlying soils and aquifers. Instead of the single composite liner required by RCRA, landfills often use double composite liners, which consist of two layers of a geotextile/compacted clay

³⁴ SWANA, 2004, p. 14 and pp. 63-64.

³⁵ For comparison, note that plastic trash bags are typically 1.1 mil, or 1.1 thousandths of an inch thick.

composite liner. Most active New Jersey landfills use double composite liners.³⁶ While the liners' construction gives confidence that they will keep their integrity, the behavior of these materials over time spans such as a hundred or a thousand years is unknown. More comprehensive models are needed to predict the long-term performance of landfill containment systems.³⁷

Modern landfills typically collect and treat leachate to remove metals, biological oxygen demand (BOD), chemical oxygen demand (COD), and bacteria before discharging the leachate to surface water, or they send the leachate to a publicly-owned treatment works (POTW). In some cases, landfills pretreat leachate. (In New Jersey, this pretreatment is usually to lower BOD and COD; no landfill has had to pretreat for metals prior to discharging to a POTW.³⁸)

When landfills have reached their capacity limits, they are "closed." Closure typically includes installation of a relatively impervious cover, grading of the surface contours of the landfill to enhance water runoff and a continuation of monitoring of groundwater with perimeter wells for 30 years. In many cases, landfills also have a gas collection and venting system, which may include combustion of the landfill gas or pumping of the gas off-site to be used as fuel.³⁹

6. Characterization of the LF environment: chemistries and associated effects on the solubilities of metals

Except for mercury, which is more volatile than the others, if heavy metals escape from a landfill, they are likely to do so primarily in the aqueous form, via **landfill leachate** or runoff that is not successfully captured by the leachate collection system.. Leachate is liquid that forms as waste decomposes, and, in some definitions at least, it includes water from rainfall that has percolated through waste or water that otherwise has come in contact with waste. Therefore, an exploration of the solubility of metals and metal compounds in leachate is relevant.

Sulfides of some metals, such as HgS (mercury sulfide), are virtually insoluble. Some oxides, e.g. CdO (cadmium oxide), Pb₃O₄, Pb₂O₃ and Pb₂O (lead oxides) are also insoluble. However, some oxides and oxygen-containing heavy metal compounds including HgO (mercury oxide), Cd(OH)₂ (cadmium hydroxide), PbO, and PbSO₄ (lead sulfate) are soluble enough so that saturated solutions of these compounds would contain

³⁶ Hausman, Nelson, 2004, , NJDEP Division of Solid and Hazardous Waste, personal communication, 8/9/04.

³⁷ Inyang, Hilary, 2004, Modeling the long-term performance of waste containment systems, Env. Sci. Technol., 328A -334A, September 1, 2004.

³⁸ Hausman, 2004, personal communication.

³⁹ Landfill gas is typically approximately 50% carbon dioxide and 50% methane, with trace quantities of other substances.

amounts in the tens of parts per million range or more.⁴⁰ Concentrations in this range would be on the order of three to five orders of magnitude higher than typical leachate concentrations, as discussed below.

It is reasonable to expect that situations in landfills that favor the formation of oxidized compounds would lead to some, perhaps significant, dissolution of some heavy metal-containing compounds in leachate. So, an assessment of the nature of the landfill environment on the oxidation/reduction scale is important.

Another important characteristic of landfill chemistry is the **sorptive capacity**. For example, it is known that cations, including heavy metal cations such as Pb^{+2} and Hg^{+2} , which are the positive ions of compounds such as PbO and HgO , bind strongly to organic matter. Organic matter has a large capacity to adsorb such cations. Well-developed humus, for example, is reported to have a cation exchange capacity in the range of 150 to 300 meq per 100 grams,⁴¹ which is far higher than clays and other soil materials. The greater the sorptive capacity of the landfill environment, the more likely metals are to be tightly bound, and the less likely they are to be dissolved in the leachate and have the potential to be released from the landfill.

Another important characteristic is the **pH level**; lower pH values (acidic conditions) will tend to increase the solubilities of metals. The mechanism for this increased solubility is in part the displacement of cations on the soil adsorption sites by H^+ ions. The pH of a landfill has been found to decrease from greater than 7 to as low as pH 5 in the first year or so after waste has been deposited. This lowering of the pH is due to the production of organic acids as byproducts of fermentation, which begins after the oxygen initially present in the deposited waste is depleted. After this time, which corresponds to the acid stage (Stage II) in the chart above, the pH is expected to rise again, as acetogenic bacteria convert these acids (and alcohols) to acetate, hydrogen, and carbon dioxide. It is reported that the pH typically declines from its initial value of approximately 7 to about 5 by 100 to 200 days after the waste is first deposited, and then begins to rise until it is above 7 by perhaps 400 days after the waste is first deposited. After that, the pH is expected to very gradually decline⁴² although it is not clear how low it will eventually go.

As noted above, over the long term a landfill is hypothesized to progress through stages VI through VIII, the air intrusion, carbon dioxide, and soil air stages. In these stages, a landfill would become steadily more aerobic, and what organic matter may remain that is subject to degradation could become oxidized through aerobic biological activity, resulting in the release of carbon dioxide, which could lower the pH again. In these stages, metals not bound to remaining organic matter could become subject to oxidation and dissolution into leachate. Kjeldsen, et al. point out that there are other substances likely to be present in these later stages that would adsorb metals, however. These are

⁴⁰ Lide, David, 1994, *CRC Handbook of Chemistry and Physics, 75th Edition*, Physical Constants of Inorganic Compounds, pp. 4-36 to 4-114, CRC Press, Boca Raton, Ann Arbor, London, Tokyo.

⁴¹ Brady, Nyle C., 1974, *The Nature and Properties of Soils, 8th Edition*, p. 148, MacMillan Publishing Co., New York.

⁴² SWANA, 2004, p. vi

iron hydroxides and oxyhydrates formed during refuse oxidation. The authors note, based on studies referenced in their report, that these compounds are reactive and may adsorb other metals. However, it is not clear whether their adsorptive capacity would be sufficient to bind all metals over the long term.

Other researchers have also focused on the conditions that are likely to develop over the long-term. In one laboratory experiment using aqueous systems containing sulfidic solid phases⁴³ it was found that cadmium previously bound as a sulfide precipitate was released to the aqueous phase where conditions were changed from slightly anaerobic to aerobic. However, this study also discovered that this cadmium was subsequently removed from solution either by adsorption on iron hydroxides or by precipitation in the form of carbonates, with ambient groundwater pH being the controlling variable. Overall, the researchers found that the change to aerobic conditions remobilized less than 1% of the total cadmium present when pH was above 5. If the pH dropped below 5, about 5% of the initial total Cd became soluble and thus available for release.

A model developed by Bozkurt et al. also addressed long-term conditions.⁴⁴ Their model results indicated that the binding capacity of humic substances should be sufficient to bind all Cd, Cr, Pb, Zn, and Hg present in a landfill, and that humic substances could bind a smaller amount of Ca, Fe, and Al, provided that much of the organic waste remained as humic substances. Their model also predicted that the binding capacity of hydrous ferric oxides, formed by oxidation reactions in the post-methane forming phases, would be sufficient to bind three times as much of the metals that are susceptible to such binding. In addition, the model predicted that the alkalinity of typical wastes is high enough to buffer increasing concentrations of acids generated in the latter stages of a landfill's cycle, so that higher mobilization rates of heavy metals would not be expected for many thousands of years. The researchers noted significant uncertainties, however. One of these is the assumption that humic substances preferentially adsorb heavy metals rather than Ca, Al, and Fe, which are present in relatively large quantities. Another uncertainty is the binding capacity itself of humic substances. The authors assumed it is 100 meq per 100 g of humic substance. This is lower than the 150 to 300 meq per 100 g reported by Brady.⁴⁵ The authors also noted that there is virtually nothing known about the stability of organic matter over time frames of 1000 years or more. They assumed in their calculations that humic matter is depleted at the same rate that has been estimated to occur in peat bogs.

Another investigation by the same researchers⁴⁶ noted that the maintenance of conditions that slowed the intrusion of air into a landfill would be expected to slow the rate of any dissolution of metals that might occur. They predict that landfills where the waste is

⁴³ Altmann, R. Scott, and A. C. M. Bourg, 1996, Cadmium mobilization under conditions simulating anaerobic to aerobic transition in a landfill leachate-polluted aquifer, *Water, Air, and Soil Pollution*, 94, 385-392.

⁴⁴ Bozkurt, S., L. Moreno, and I. Neretnieks, 1999, Long-term processes in waste deposits, *Science of the Total Environment*, 250, 101-121.

⁴⁵ Brady, Nyle C., 1975.

⁴⁶ Bozkurt, S., L. Moreno, and I. Neretnieks, 1999, Long-term fate of organics in waste deposits and its effect on metal release, *Science of the Total Environment*, 228, 135-152.

below the water table or otherwise maintained in a water-saturated condition would be less likely to release metals. Interestingly, water-logged conditions such as those researchers recommend are analogous to conditions in the lower, anaerobic layers of natural sediments. However, although some landfills, e.g. those in some coastal environments, may have portions of their contents saturated with water periodically, for example through tidal action, water saturation is a condition that modern landfill design attempts to avoid.

In another effort, Christensen, et al.⁴⁷ looked not at landfill conditions per se, but at attenuation processes governing contaminants in leachate-affected aquifers. Although the mechanism was unclear, they found that heavy metals in most cases appear to be strongly attenuated in leachate-polluted aquifers, and that natural attenuation processes provide significant remediation, limiting the effects of leachate on groundwater to an area usually not exceeding 1000 m from the landfill. In the absence of further information, it must be considered, however, that at least some of this attenuation may be primarily due to dilution.

7. Measured concentrations of heavy metals in leachate

Measurements of leachate concentrations of heavy metals compiled by the USEPA in its “LEACH 2000” database, which represents data from over 200 landfills, can be compared with TCLP regulatory levels, with drinking water standards, and with RCRA groundwater regulations. See Table 2. Leachate concentration data for several New Jersey landfills are presented in Table 3.

Metal	No. samples	Mean (mg/l)	90 th percentile (mg/l)	TCLP level (mg/l)	EPA Primary drinking water MCL (mg/l)	RCRA groundwater MCL (mg/l)
Arsenic	2,444	0.441	0.100	5	0.01	0.05
Barium	1,779	0.866	1.700	100	2	1
Cadmium	2,351	0.283	0.079	1	0.005	0.01
Chromium	2,776	0.235	0.341	5	0.1	0.05
Lead	2,539	0.133	0.250	5	0.015	0.05
Mercury	2,078	0.00715	0.0046	0.2	0.002	0.002
Selenium	1,754	0.585	0.180	1	0.05	0.01
Silver	1,830	0.0537	0.056	5	NA	0.05

⁴⁷ Christensen, Thomas, P. Kjeldsen, P. Bjerg, D. Jensen, J. Christensen, A. Baun, H-J Albrechtsen, and G. Heron, 2001, Biogeochemistry of landfill leachate plumes, *Applied Geochemistry*, 16, 659-718.

⁴⁸ SWANA, 2004, Tables ES-2, p. 2, and ES-5, p. 4.; NOTE, the drinking water standard for As is reported in the referenced document as 0.05 mg/l. The federal standard has recently been lowered to 0.01 mg/l (10 ppb), and some jurisdictions, including New Jersey, are considering lowering the standard to 5 ppb or less.

Table 3. Leachate heavy metal concentrations from four NJ landfills				
Landfill	Metal	Mean (mg/l)	No. samples	No. non-detects
Cape May Co.	Arsenic	0.055	16	1
	Cadmium	0.003	8	8
	Lead	0.003	16	16
	Mercury	0.00009	8	8
Cumberland Co.	Arsenic	0.0074	27	15
	Cadmium	0.002	27	27
	Chromium	0.015	27	1
	Copper	0.059	27	0
	Lead	0.0025	27	27
	Mercury	0.00005	27	27
	Nickel	0.121	27	1
	Zinc	0.051	27	0
Pinelands Park	Cadmium	0.0053	11	3
	Chromium	0.037	11	0
	Lead	0.026	11	2
	Nickel	0.067	48	5
	Zinc	0.195	11	0
Sharkey LF	Arsenic	0.011	16	0
	Cadmium	0.0003	16	12
	Chromium	0.0098	16	0
	Lead	0.0042	16	1
	Mercury	0.0001	3	0
	Nickel	0.052	16	0

The leachate concentrations in Table 2, reflecting data from a variety of landfills in the U.S., generally exceed, except for Barium, drinking water standards and groundwater maximum contaminant levels (MCLs). Arsenic and cadmium stand out by exceeding the MCLs by wide margins; both have mean concentrations more than 40 times higher than drinking water MCLs. Some states, e.g. New Jersey, have imposed an arsenic MCL of 0.005 mg/l; the mean arsenic leachate concentration is more than 80 times higher than this standard.

The Sharkey LF shown in Table 3 is a NPL (Superfund) site. The concentration values presented for this landfill are from the groundwater extraction system, not leachate. This landfill is reported to have opened around 1945, and to have closed in the 70s or early 80s. Of the other three landfills, Cape May Co. and Cumberland Co. are active, state-of-

the-art sites that opened in the mid-80s. Their leachate is sent off site to a POTW. The Pinelands Park landfill is believed to have opened around 1970. It closed in 1990.

The values in Table 3, from four New Jersey landfills, appear generally lower than those values in LEACH 2000 as cited in Table 2, although some values, particularly for As, are higher than drinking water standards. These values represent average concentrations as reported in New Jersey DEP databases, and, as presented here, were calculated by estimating non-detect values to be one half the detection limit. No New Jersey landfills are included in the LEACH 2000 database.

These data demonstrate that leachate must be kept isolated from groundwater, and must be treated to remove high concentrations of metals before it is discharged to surface waters. Existing regulations, including requirements for landfill containment systems as discussed above, are designed to ensure that untreated leachate does not pollute surface or ground waters. Should a landfill's containment system fail at some point, however, the relatively high concentrations of heavy metals such as arsenic and cadmium in leachate indicate that ground waters or surface waters could be threatened. Pollution of water resources by landfills could be especially problematic in situations where leachate could directly impact surface waters or groundwater systems, such as in landfills sited above fractured rock or cavernous limestone aquifer systems.⁴⁹

A particular concern about arsenic and cadmium is heightened by the likelihood that more arsenic-containing and cadmium-containing material will be deposited in landfills in future years. Many water purveyors will have to treat water to remove arsenic to keep water below the MCL of 0.01 mg/l, which becomes effective at the national level in 2006. A byproduct of such treatment is arsenic-containing filter media, which may be disposed of in landfills.

Although it is beyond the scope of this paper, concerns have been expressed that the TCLP test, the results of which can determine whether a waste is considered hazardous, is not representative of the actual leaching behavior of some arsenic in a landfill environment.⁵⁰ More thorough screening of waste, particularly waste suspected of containing relatively large amounts of arsenic, to ensure that it is safely disposed appears appropriate in the future.

As shown in Figure 1, above, some data indicate that the cadmium concentration of MSW is increasing. Review of metals concentrations of ash from a New Jersey incinerator suggests that the cadmium concentration of MSW has increased from approximately 10 ppm in the early 1990s to approximately 20 ppm in 2004. It is likely that increased disposal of cadmium-containing batteries in consumer electronic devices, such as cell phones, is driving this increase. Although the consumer electronics industry

⁴⁹ Lee, 2004.

⁵⁰ Ghosh, Amlan, M. Muikiibi, and Wendell Ela, 2004, TCLP underestimates leaching of arsenic from solid residuals under landfill conditions, *Environ. Sci. Technol.* 38, 4677-4682.

has made some attempt to encourage recycling of spent cadmium-containing batteries (typically nickel-cadmium, or Ni-Cd, batteries), it appears that much more needs to be done to keep Ni-Cd batteries out of the waste stream. See the report on pollution prevention and management strategies for cadmium by the New York Academy of Sciences.⁵¹

In New Jersey, leachate levels of at least one metal, mercury, appear low enough to be of little concern from a statewide emissions perspective. Using conservative assumptions (conservative in this case means high), that leachate mercury concentration was 5 µg/l and that most landfills allowed significant infiltration of water and thus produced significant quantities of leachate, it was estimated that, in New Jersey, landfills would discharge on the order of 50 kg of mercury per year in the form of leachate.⁵² This quantity is less than many other sources of mercury to the New Jersey environment. However, it must be noted that no assumptions were made about which chemical forms of mercury are typical in leachate. Results have been reported as total mercury only. A similar exercise, although quite speculative, can be performed using the LEACH 2000 database to estimate total national releases of metals from landfills. Such an exercise could assume that, based on population, national quantities are 33 times greater than NJ quantities, and that similar assumptions about rainfall and degree of infiltration and hence leachate production apply. Using mean leachate concentrations from the LEACH 2000 database, this set of calculations leads to estimates of the following U.S. emissions quantities, in metric tons (T) per year: arsenic, 145 T; barium, 286T; cadmium, 93T; chromium, 77T; lead, 44T; mercury, 2.4T; selenium, 193T; and silver, 18T.

These quantities appear relatively low compared to other sources. For example, 2003 releases from U.S. TRI facilities totaled 131,000 T, 3,000 T, 32,000 T, and 194,000 T for arsenic & its compounds, cadmium & compounds, chromium & compounds, and lead & compounds, respectively.⁵³ However, it must be noted that no information is available on the species of these emissions. If, for example, a significant portion of a metal emitted to a water body from a landfill was methylated, e.g., methyl mercury, a relatively small emission could nevertheless be important.

8. Measured air emissions of heavy metals

Gaseous emissions from landfills are typically composed of approximately 50% methane and 50% carbon dioxide, with trace quantities of other gases, such as hydrogen sulfide. The trace gas emissions include elemental mercury or mercury-containing compounds. Mercury is the only heavy metal reported in gaseous emissions from landfills. Measured levels have consistently been low enough to suggest little cause for concern. It is

⁵¹ Boehme, Susan and M Panero, 2003.

⁵² NJDEP, 2002, NJ Mercury Task Force, Vol III, p. 159.

⁵³ USEPA, 2006, Toxic Release Inventory, total on and off-site disposal or other releases, as downloaded from <http://www.epa.gov/triexplorer/>, 1/26/06.

reported that, in New Jersey, where landfill gas concentrations have been measured for several landfills pursuant to permit requirements, the mean concentration of mercury is between 5 and 10 $\mu\text{g}/\text{m}^3$. Multiplying the mid-point of this range by the total estimated volume of landfill gas estimated to be emitted in that state led to an estimate of a yearly mercury emission on the order of 15 kg in the year 2000. This is a relatively small portion of the total estimated statewide mercury emission to the air that year of perhaps 2000 kg.

No information is available on the species of mercury emitted from NJ landfills; all concentrations have been expressed as total mercury. Some concern has been raised that a significant portion of landfill mercury emissions might be methylated species that are easily taken up by organisms and are known to be highly toxic. It is also theoretically possible that other metals, such as arsenic, could be transformed in a landfill into organic forms volatile enough to escape to the atmosphere. A recent study found 50 ng of dimethyl mercury per cubic meter of landfill gas.⁵⁴ Assuming this quantity was typical, and multiplying it by the total estimated emission of landfill gas led to an estimate of a total emission of about 85 grams per year in New Jersey.⁵⁵ Gaseous organic forms of mercury likely are quickly oxidized in the atmosphere to inorganic forms; combustion of landfill gas will also convert organic mercury to inorganic forms. Overall, gaseous emissions of mercury from New Jersey landfills appear to be relatively insignificant.

9. Conclusions

No data exist that can definitively answer all questions about the long-term behavior of heavy metals in landfills. Without such data, the concern cannot be dismissed that there might come a point in time when the reservoirs of heavy metals in landfills might be transformed to soluble species and released. However, available data from landfills that have been functioning as long as 60 years have provided no evidence of increasing leachate concentrations of metals over time.

Modeling of long-term behavior of landfills has so far not suggested that landfills will change over the long-term enough to release significant amounts of their stores of heavy metals. However, more comprehensive modeling, including representation of conditions expected to exist in arid areas and also humid, relatively acidic conditions such as may exist in the southeastern U.S., and comparison of modeled results with existing trends of landfill emissions is warranted. More data is also needed on the long-term behavior of containment systems.

⁵⁴ Lindberg, S., D. Wallschlager, E. Prestbo, N. Bloom, J. Price, and D. Reinhart, 2001, Methylated mercury species in municipal waste landfill gas sampled in Florida, USA, *Atmospheric Environment*, 35, 4011-4015.

⁵⁵ NJDEP, 2002, NJ Mercury Task Force, Vol III, p. 157.

Finally, even if these models were to convincingly demonstrate that heavy metals are very likely to be sequestered in landfills in the long-term, there are many reasons to reduce the amount of MSW sent to landfills, primarily that space for these facilities is limited, and construction costs of building new plants are high. Furthermore, from the perspective of total management of the waste stream, it is important to adhere to certain MSW policies (e.g., reuse, material separation and recovery) because these practices can divert the amount of material that is sent not only to landfills but also to incinerators and Waste to Energy Facilities.⁵⁶

⁵⁶ Releases from WTE are not treated in this paper and are likely to be higher than those from landfills.